

Claims

1. A method for preparing an unsaturated carboxylic acid from the corresponding aldehyde, which
5 comprises a step for oxidizing said aldehyde, in a controlled basic medium and using molecular oxygen or a gas containing it, in the presence of a catalyst based on palladium and/or platinum and of an activator based on bismuth, under conditions
10 such that the oxidation occurs in a diffusion mode.
2. The method as claimed in claim 1, wherein the starting aldehyde is an aliphatic or
15 cycloaliphatic aldehyde having at least one unsaturation, a double bond or a triple bond.
3. The method as claimed in claim 2, wherein the starting aldehyde is an aliphatic aldehyde having
20 two double bonds of which at least one is conjugated with the carbonyl group.
4. The method as claimed in one of claims 1 to 3, wherein the starting aldehyde is a terpene
25 aldehyde.
5. The method as claimed in claim 1, wherein the starting aldehyde corresponds to formula (I):
A-CHO (I)
30 in said formula (I):
- A represents a hydrocarbon group having at least one unsaturation having from 4 to 19 carbon atoms which may be a linear or branched, saturated or unsaturated acyclic aliphatic group; a monocyclic
35 or polycyclic, saturated or unsaturated or aromatic carbocyclic group; a linkage of a saturated or unsaturated aliphatic group and/or of a saturated, unsaturated or aromatic carbocycle.

6. The method as claimed in claim 5, wherein the aldehyde corresponds to formula (I) in which A represents a linear or branched acyclic aliphatic group preferably having from 4 to 19 carbon atoms comprising one or more unsaturations in the chain, generally 1 to 5 unsaturations which may be single or conjugated double bonds or triple bonds: it being possible for the unsaturation to be at the chain end and/or alternatively inside the chain and/or conjugated with the CO group.
7. The method as claimed in claim 6, wherein the aldehyde corresponds to formula (I) in which A represents a linear or branched alkyl group having from 4 to 19 carbon atoms and comprising at least one double bond, preferably two double bonds of which at least one is conjugated with the CO group.
8. The method as claimed in claim 5, wherein the aldehyde corresponds to formula (I) in which A represents a carbocycle having from 3 to 8 carbon atoms in the ring, preferably 5 or 6 and comprising 1 or 2 unsaturations in the ring, preferably 1 or 2 double bonds.
9. The method as claimed in claim 8, wherein the aldehyde corresponds to formula (I) in which A represents a cycloalkyl group having from 3 to 8 carbon atoms, preferably 5 or 6 and comprising a double bond.
10. The method as claimed in claim 5, wherein the aldehyde corresponds to formula (I) in which A represents a polycyclic carbocyclic group comprising from 3 to 6 carbon atoms in each ring and of which at least one of the rings comprises one unsaturation; it being possible for the other ring to be saturated or aromatic.

11. The method as claimed in claim 1, wherein the starting aldehyde is citral, prenal retinal, cyclocitral, safranal.
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12. The method as claimed in claim 1, wherein the platinum and/or palladium catalyst is provided in the form of platinum black, palladium black, platinum oxide, palladium oxide or the noble metal itself deposited on various supports such as carbon black, graphite, activated charcoal, activated aluminas and silicas or equivalent materials, preferably carbon black.
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13. The method as claimed in claim 1, wherein the quantity of catalyst to be used, expressed by weight of metal M_1 relative to that of the compound of formula (I), varies from 0.001 to 10%, and preferably from 0.002 to 2%.
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14. The method as claimed in claim 1, wherein the activator is an organic or inorganic derivative of bismuth chosen from the group consisting of: bismuth oxides; bismuth hydroxides; bismuth or bismuthyl salts of inorganic hydracids, preferably the chloride, bromide, iodide; bismuth or bismuthyl salts of inorganic oxyacids, preferably the sulfite, sulfate, nitrite, nitrate, phosphite, phosphate; pyrophosphate, carbonate, perchlorate; the bismuth or bismuthyl salts of aliphatic or aromatic organic acids, preferably the acetate, propionate, salicylate, benzoate, oxalate, tartrate, lactate, citrate.
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15. The method as claimed in claim 14, wherein the bismuth derivative is chosen from the group consisting of: bismuth oxides Bi_2O_3 and Bi_2O_4 ; bismuth hydroxide $Bi(OH)_3$; bismuth chloride $BiCl_3$; bismuth bromide $BiBr_3$; bismuth iodide BiI_3 ; neutral
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bismuth sulfate $\text{Bi}_2(\text{SO}_4)_3$; neutral bismuth nitrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$; bismuthyl carbonate $(\text{BiO})_2\text{CO}_3 \cdot 0.5\text{H}_2\text{O}$; bismuth acetate $\text{Bi}(\text{C}_2\text{H}_3\text{O}_2)_3$; bismuthyl salicylate $\text{C}_6\text{H}_4\text{CO}_2(\text{BiO})\text{OH}$.

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16. The method as claimed in claim 15, wherein the quantity of activator expressed by weight of bismuth relative to the weight of the metal M_1 used varies between 1 and 200% and is preferably
10 in the region of 100%.
17. The method as claimed in claim 1, wherein the basic agent used is sodium hydroxide or potassium hydroxide.
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18. The method as claimed in claim 1, wherein the quantity of base introduced into the reaction medium is such that the ratio between the number of moles of OH^- and the number of moles of aldehyde varies between 0.9 and 1.1, and is
20 preferably equal to about 1.
19. The method as claimed in claim 1, wherein the quantity of water in the reaction medium should be
25 sufficient to solubilize the salt of the acid formed.
20. The method as claimed in claim 1, wherein the oxidation temperature is chosen between 20°C and
30 60°C , preferably between 30°C and 40°C .
21. The method as claimed in claim 1, wherein the pressure is atmospheric pressure.
- 35 22. The method as claimed in claim 1, wherein the stirring conditions are such that the reaction mode is a diffusion mode.
23. The method as claimed in claim 1, which consists

in introducing the water, the basic agent, the catalyst based on palladium and/or platinum, the activator, and then finally the aldehyde to be oxidized.

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24. The method as claimed in claim 23, wherein the metal M_1 is reduced with formalin.

10 25. The method as claimed in either of claims 22 and 23, wherein the reaction mixture maintained under a stream of inert gas (preferably nitrogen) is heated to the desired reaction temperature and then oxygen or a gas containing it is introduced.

15 26. The method as claimed in claim 25, wherein the medium is stirred at the desired temperature until a quantity of oxygen corresponding to that necessary to convert the formyl group to a carboxyl group is consumed.

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27. The method as claimed in claim 1, wherein the carboxylic acid formed after an acid treatment is recovered.